

Docket No.: 1155-0311PUS1
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Yasushi TOHI et al.

Application No.: 10/550,021

Confirmation No.: 3856

Filed: September 23, 2005

Art Unit: 1713

For: PROCESS FOR PRODUCING OLEFIN
POLYMERS

Examiner: C. C. Lu

LETTER SUBMITTING TRANSLATION OF PRIORITY DOCUMENT

MS RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Attached is the true and complete translation of Japanese Patent Application No. 2004-105387.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Craig A. McRobbie, Reg. No. 42,874, at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37.C.F.R. §§1.16 or 1.14; particularly, extension of time fees.

Dated: October 31, 2007

Respectfully submitted,

By  #42874

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DECLARATION

We, MITSUI CHEMICALS, INC., of Shiodome City Center, 5-2, Higashi-Shimbashi 1-chome, Minato-ku, Tokyo, Japan, do hereby certify to the best of our knowledge, information and belief that the annexed specification is a true and complete translation in English of the specification as filed in connection with the Japanese Patent Application No. 2004-105387.

Dated this 28 day of September, 2007

MITSUI CHEMICALS, INC.

Signature: Taira Harada

- 1 -

[Name of Document] Application for Patent
[Reference No.] P0003149
[Submission date] March 31, 2004
[Destination] Commissioner, Patent Office
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[Designation of Charge]
20 [Ledger No. for Prepayment] 005278
[Amount of Payment] 21,000 Yen
[List of Document Submitted]
[Object Name] Claims 1
[Object Name] Specification 1
25 [Object Name] Abstract 1

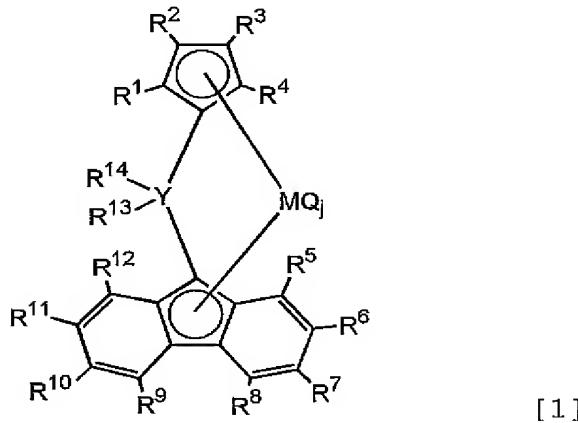
[Name of Document] Claims

[Claim 1]

A process for producing an olefin polymer, which comprises polymerizing one or more kinds of monomers 5 selected from ethylene and α -olefins at a temperature of 120°C or higher, in the presence of a catalyst for olefin polymerization consisting of:

(A) a Group IVB transition metal compound represented by the following general formula [1]:

10 [Chemical Formula 1]



(wherein R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹ and R¹² are each selected from hydrogen, a hydrocarbon group, and a silicon-containing group, and may be the same or different 15 from each other; R¹³ and R¹⁴ are selected from a halogen-containing hydrocarbon group, a hydrocarbon group, a halogen atom, an oxygen-containing group, a nitrogen-containing group and a silicon-containing group; or R¹³ and R¹⁴ may be bonded together to form a ring; or the neighboring

substituents represented by R¹ to R¹² may be bonded together to form a ring; M is Ti, Zr or Hf; Y is carbon; Q may be selected from halogen, a hydrocarbon group, an anionic ligand and a neutral ligand that can be coordinated with a lone electron pair, combined in the same or different combinations; and j is an integer from 1 to 4); and

(B) at least one compound selected from the group consisting of

(B-1) an organoaluminum oxy compound,

(B-2) a compound which reacts with the Group IVB transition metal compound (A) to form an ion pair, and

(B-3) an organoaluminum compound.

[Claim 2]

The process for producing an olefin polymer according to claim 1, which uses the catalyst comprising the metallocene compound, wherein in the formula [1], any at least two substituents of R⁶, R⁷, R⁸, R⁹, R¹⁰ and R¹¹ are each a hydrocarbon group having a total of 1 to 20 carbon atoms or a silicon-containing group, and the neighboring substituents may be bonded together to form a ring.

[Claim 3]

The process for producing an olefin polymer according to claim 1, which uses the catalyst comprising the metallocene compound, wherein in the formula [1], R¹³ and R¹⁴ are each a substituted aryl group having at least one

substituent selected from a halogen-containing hydrocarbon group, a hydrocarbon group, a halogen atom, an oxygen-containing group, a nitrogen-containing group and a silicon-containing group, combined in the same or different
5 combinations, or an unsubstituted aryl group, and R¹³ and R¹⁴ may be the same or different from each other.

[Name of Document] Specification

[Title of the Invention] Process for Producing Olefin Polymer

[Technical Field of the Invention]

5 [0001]

The present invention relates to a process for polymerization of an olefin, wherein the olefin is polymerized in the presence of a catalyst containing a metallocene compound having a specific structure at 120°C.

10 [Description of the Related Art]

[0002]

The process of polymerization of an olefin in the presence of a metallocene-based catalyst which consists of a transition metal compound such as zirconocene and an 15 organoaluminum oxy compound (aluminoxane) is reported by W. Kaminsky, et al. as a representative example (Adv. Organomet. chem. 1899 (1980)). Regarding the process for stereospecific polymerization of an α -olefin, further improvements are desired from the standpoint of the 20 polymerization activity or stereospecificity, which has been considerably improved since isotactic polymerization was reported by W. Kaminsky, et al. (Angew. Chem. Int. Ed. Engl., 24. 507 (1985)). As a part of such studies, propylene polymerization using a metallocene compound bridged with a 25 cyclopentadienyl ligand and a fluorenyl ligand is reported

by J. A. Ewen (J. Am. Chem. Soc., 110, 6255 (1988)). It is known that by using these metallocene-based catalysts, an olefin can be polymerized with high activity, and further an olefin (co)polymer having narrow molecular weight distribution and narrow composition distribution can be obtained.

[0003]

Recently, regarding the requirements of the properties of an olefin (co)polymer, an olefin (co)polymer having various properties is desired, and development of a catalyst for olefin polymerization satisfying the above requirements is desired.

[0004]

Under these circumstances, a process for producing an ethylene/1-hexene copolymer with a relatively high density using dicyclopentadienylzirconium dichloride, which is a transition metal compound containing a cyclopentadienyl group as a ligand and methyl aluminoxane under the condition of high pressure and high temperature is described in JP-A No. 01-503788. Further, a process for producing an ethylene/1-octene copolymer at high temperature using dicyclopentadienylzirconium dichloride and dimethylanilinium tetra(pentafluorophenyl)boron was described in JP-A No. 5-320246. However, these processes have a problem that it was impossible to obtain a high molecular weight polymer in the

low-density region (that is, in the region where the comonomer content is high) since the processes can give only a polymer with low polymerization activity and low molecular weight. Thus, it is presumed that the rigidity or strength required upon using the polymer as a resin is insufficient.

5 [Patent-Document 1] JP-A No. 1-503788

[Patent-Document 2] JP-A No. 5-320246

[Non Patent-Document 1] Adv. Organomet. chem. 1899
(1980)

10 [Non Patent-Document 2] Angew. Chem. Int. Ed. Engl.,
24. 507 (1985)

[Non Patent-Document 3] J. Am. Chem. Soc., 110, 6255
(1988)

[Disclosure of the Invention]

15 [Problems to be Solved by the Invention]

[0005]

To solve the problems, a means for improving the molecular weight by lowering the polymerization temperature and inhibiting the chain transfer reaction which occurs upon 20 polymerization, can be considered. However, in this case, if polymerization occurs at a temperature below the melting point of the polymer, the polymer would be precipitated, thereby causing the lowering of the stirring efficiency and the dramatic reduction of productivity. Moreover, there is 25 also a problem that at low temperatures, the conversion rate

of a co-monomer is low and the density cannot be sufficiently reduced. For these reasons, the stirring efficiency is not lowered by performing the polymerization in the solution state at a polymerization temperature above 5 the melting point of the polymer and in the solution state. Moreover, it is convenient to control the reaction by easing heat removal upon the polymerization. Further, the conversion rate of a co-monomer is high and the density can be lowered. Accordingly, development of a catalyst capable 10 of polymerizing a high molecular weight polymer under the polymerization condition of high temperature is desired.

[0006]

The invention was made in order to solve the above-described problems, and thus, according to the invention, a 15 high molecular weight polymer can be obtained with high polymerization activity under the polymerization condition of high temperature, and particularly, the invention provides a process for producing an olefin polymer having a high comonomer content, a narrow composition distribution, 20 and a narrow molecular weight distribution.

[Means for Solving the Problems]

[0007]

It was found that according to the invention, a high molecular weight polymer, and in particular, an olefin 25 polymer with a high comonomer content, a narrow composition

distribution and a narrow molecular weight distribution can be obtained by copolymerization of one or more kinds of monomers selected from ethylene and α -olefins even under the condition of a high polymerization temperature of 120°C or
5 higher.

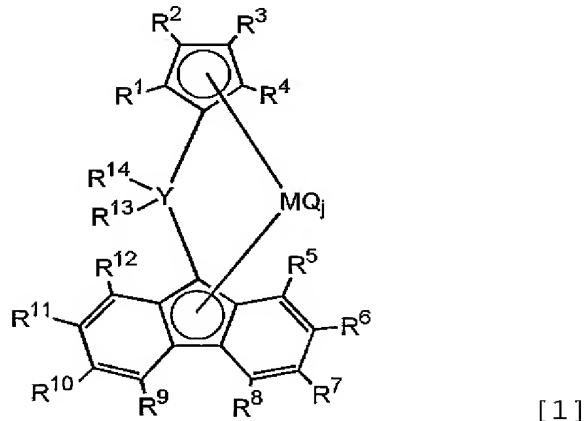
[0008]

The invention is a process for producing an olefin polymer, which comprises polymerizing one or more kinds of monomers selected from ethylene and α -olefins at a
10 temperature of 120°C or higher, in the presence of a catalyst for olefin polymerization consisting of:

(A) a Group IVB transition metal compound represented by the following general formula [1]:

[0009]

15 [Chemical Formula 1]



[0010]

(wherein R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹ and R¹² are each selected from hydrogen, a hydrocarbon group, and a

silicon-containing group, and may be the same or different from each other; R¹³ and R¹⁴ are selected from a halogen-containing hydrocarbon group, a hydrocarbon group, a halogen atom, an oxygen-containing group, a nitrogen-containing

5 group and a silicon-containing group; or R¹³ and R¹⁴ may be bonded together to form a ring; or the neighboring substituents represented by R¹ to R¹² may be bonded together to form a ring; M is Ti, Zr or Hf; Y is carbon; Q may be selected from halogen, a hydrocarbon group, an anionic
10 ligand and a neutral ligand that can be coordinated with a lone electron pair, combined in the same or different combinations; and j is an integer from 1 to 4); and
(B) at least one compound selected from the group consisting of

15 (B-1) an organoaluminum oxy compound,
(B-2) a compound which reacts with the Group IVB transition metal compound (A) to form an ion pair, and
(B-3) an organoaluminum compound.

[Effect of the Invention]

20 [0011]

According to the invention, a high molecular weight polymer can be obtained with high activity under the polymerization condition of high temperature, and the copolymer has the characteristics of a high comonomer
25 content, a narrow composition distribution and a narrow

molecular weight distribution.

[Best Mode for Carrying out the Invention]

[0012]

The monomer used for olefin polymerization of the
5 invention is one or more kinds of monomers selected from ethylene and α -olefins, wherein at least one of the monomers is ethylene or propylene. The polymerization reaction is carried out in the presence of a catalyst for olefin polymerization containing the bridged metallocene compound
10 represented by the formula [1] which has the following characteristics of the chemical structure, 1) to 3).

1) Of the two ligands, one ligand is a cyclopentadienyl group, and the other ligand is a fluorenyl group, wherein the fluorenyl group is a substituted fluorenyl group.

15 2) The two ligands are linked by a covalent-bond bridge which contains a carbon atom.

3) The transition metal which constitutes the metallocene compound is titanium, zirconium, or hafnium.

[0013]

20 Hereinbelow, a cyclopentadienyl group which may be substituted or unsubstituted, and a substituted fluorenyl group, wherein in the formula [1], R⁵ to R¹² are not hydrogen atoms at the same time, each of which constitutes the characteristics of the chemical structure of the bridged
25 metallocene compound of the invention, will be explained

successively; and then preferable bridged metallocene compounds which have such the characteristics and examples thereof, a method for producing the bridged metallocene compound according to the invention, and finally preferable 5 embodiments or polymerization methods in the case of providing the bridged metallocene compound according to the invention as a catalyst for olefin polymerization will be explained.

[0014]

10 Cyclopentadienyl group which may be substituted or unsubstituted

One or plural (more than one) hydrogen atom of a cyclopentadienyl group used for the metallocene compound which is used in the polymerization method of the invention, 15 may be substituted or unsubstituted. In the case where it is substituted, the substituents may be exemplified by a hydrocarbon group having a total of 1 to 20 carbon atoms, and a silicon-containing group. In the case where plural hydrogen atoms are substituted, the substituents may be the 20 same or different from each other. Further, the hydrocarbon group having a total of 1 to 20 carbon atoms includes, in addition to alkyl, alkenyl, alkynyl, and aryl groups which consist of carbon and hydrogen only, the hydrocarbon group in which parts of the hydrogen atoms directly bonded to such 25 carbon atoms are substituted with a halogen atom, an oxygen-

containing group, a nitrogen-containing group, or a silicon-containing group, and the hydrocarbon group in which any two neighboring hydrogen atoms are both substituted to form an alicyclic or aromatic group. The silicon-containing group
5 refers to, for example, a group in which the ring-carbon of the cyclopentadienyl group is directly bonded to a silicon atom via a covalent bond, and specifically to an alkylsilyl group or an arylsilyl group.

[0015]

10 Examples of the hydrocarbon group having a total of 1 to 20 carbon atoms as the substituent include a straight-chain hydrocarbon group such as a methyl group, an ethyl group, an n-propyl group, an allyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an
15 n-octyl group, an n-nonyl group, and an n-decanyl group; a branched hydrocarbon group such as an isopropyl group, a t-butyl group, an amyl group, a 3-methylpentyl group, a 1,1-diethylpropyl group, a 1,1-dimethylbutyl group, a 1-methyl-1-propylbutyl group, a 1,1-propylbutyl group, a 1,1-dimethyl-2-methylpropyl group, and a 1-methyl-1-isopropyl-2-methylpropyl group; a cyclic saturated hydrocarbon group such as a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a norbornyl group, and an adamantyl group; a cyclic unsaturated hydrocarbon
20 group such as a phenyl group, a naphthyl group, a biphenyl
25

group, a phenanthryl group, and an anthracenyl group; a saturated hydrocarbon group substituted with an aryl group such as a benzyl group, and a cumyl group; an oxygen-containing hydrocarbon group such as a methoxy group, an 5 ethoxy group and a phenoxy group; and a nitrogen-containing hydrocarbon group such as an N-methylamino group, an N,N-dimethylamino group and an N-phenylamino group.

[0016]

Examples of the halogen atom as the substituent include 10 a fluorine atom, a chlorine atom, a bromine atom and an iodine atom. Further, examples of the silicon-containing group as the substituent include a trimethylsilyl group, triethylsilyl group and the like.

[0017]

15 Substituted fluorenyl group

The important point of the substituted fluorenyl group used for the metallocene compound which is used in the polymerization method of the invention is that R⁵ to R¹² in the above general formula [1] are not hydrogen atoms at the 20 same time. By the substitution of any at least one hydrogen atom of the fluorenyl group, high polymerization activity is exhibited. Examples of the substituent include a hydrocarbon group having a total of 1 to 20 carbon atoms and a silicon-containing group. In the case where plural 25 hydrogen atoms are substituted, the substituents may be the

same or different from each other. Further, the hydrocarbon group having a total of 1 to 20 carbon atoms includes, in addition to alkyl, alkenyl, alkynyl, and aryl groups which consist of carbon and hydrogen only, the hydrocarbon groups 5 in which parts of the hydrogen atoms directly bonded to such carbon atoms are substituted with a halogen atom, an oxygen-containing group, a nitrogen-containing group, or a silicon-containing group, or the hydrocarbon groups in which any two neighboring hydrogen atoms are both substituted to form an 10 alicyclic or aromatic group. Further, the silicon-containing group refers to, for example, the group in which the ring-carbon of the cyclopentadienyl group is directly bonded to a silicon atom via a covalent bond, and specifically to an alkylsilyl group or an arylsilyl group.

15 A preferable embodiment of the substituted fluorenyl group is the group in which any at least two substituents of R₆, R₇, R₈, R₉, R₁₀ and R₁₁ in the above general formula [1] are a hydrocarbon group having a total of 1 to 20 carbon atoms or a silicon-containing group. Further, from the 20 viewpoint of the easy production of the metallocene compound and the olefin polymerization activity, it is preferable that R⁶ and R¹¹ are identical groups, or R⁷ and R¹⁰ are identical groups. More preferred are the compound in which R₆ and R₁₁ are substituted, the compound in which R₇ and R₁₀ 25 are substituted, or the compound in which R₆, R₇, R₁₀ and

R11 are substituted with four substituents. Specific examples of the compound in which R6 and R11 are substituted include 2,7-di-tert-butylfluorene, examples of the compound in which R7 and R10 are substituted include 3,6-di-tert-
5 butylfluorene and examples of the compound in which R6, R7, R10 and R11 are substituted with four substituents include octamethyloctahydrodibenzofluorene and the like.

[0018]

Carbon atom-containing covalent-bond bridge

10 The main chain part of the bond which links the cyclopentadienyl group and the fluorenyl group is a divalent covalent-bond bridge which contains a carbon atom. Further specifically, examples of the bridged part include a saturated hydrocarbon group having a total of 2 to 20 carbon
15 atoms such as $-\text{CH}_2-$, $-\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$, a cyclohexylidene group and a cyclopentylidene group, and an unsaturated hydrocarbon group having a total of 6 to 20 carbon atoms such as $-\text{CH}(\text{C}_6\text{H}_5)-$, $-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)-$ and $-\text{C}(\text{C}_6\text{H}_5)_2-$. Among these, in a preferred embodiment of the bridged part, at least one
20 of R¹³ and R¹⁴ in the above general formula [1] is preferably substituted or unsubstituted aryl.

[0019]

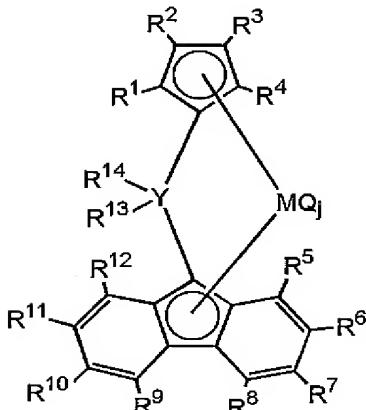
Preferable bridged metallocene compound and examples thereof

25 The metallocene compound of the invention is a

transition metal compound having the structure represented by the following general formula [1].

[0020]

[Chemical Formula 2]



5

[1]

[0021]

In the formula [1], R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³ and R¹⁴ are each selected from hydrogen, a hydrocarbon group, and a silicon-containing group, and may be the same or different from each other; R⁵ to R¹² are not hydrogen atoms at the same time; M is Ti, Zr or Hf, and preferably Zr or Hf; Y is carbon; Q may be selected from halogen, a hydrocarbon group, an anionic ligand and a neutral ligand that can be coordinated with a lone electron pair, combined in the same or different combinations; and j is an integer from 1 to 4.

[0022]

R¹ to R¹⁴, Y and M are as described above. In the formula [1], Q is selected from halogen, a hydrocarbon group

having 1 to 10 carbon atoms, a neutral, conjugated or non-conjugated diene having 10 carbon atoms or less, an anionic ligand, and a neutral ligand that can be coordinated with a lone electron pair, combined in the same or different combinations. Specific examples of the halogen include fluorine, chlorine, bromine, and iodine; and specific examples of the hydrocarbon group include methyl, ethyl, n-propyl, isopropyl, 2-methylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1,1-diethylpropyl, 1-ethyl-1-methylpropyl, 1,1,2,2-tetramethylpropyl, sec-butyl, tert-butyl, 1,1-dimethylbutyl, 1,1,3-trimethylbutyl, neopentyl, cyclohexylmethyl, cyclohexyl, 1-methyl-1-cyclohexyl, and the like. Specific examples of neutral, conjugated, or non-conjugated diene having 10 or less carbon atoms include s-cis- or s-trans- η^4 -1,3-butadiene, s-cis- or s-trans- η^4 -1,4-diphenyl-1,3-butadiene, s-cis- or s-trans- η^4 -3-methyl-1,3-pentadiene, s-cis- or s-trans- η^4 -1,4-dibenzyl-1,3-butadiene, s-cis- or s-trans- η^4 -2,4-hexadiene, s-cis- or s-trans- η^4 -1,3-pentadiene, s-cis- or s-trans- η^4 -1,4-ditolyl-1,3-butadiene, s-cis- or s-trans- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene, and the like. Specific examples of anionic ligand include an alkoxy group such as methoxy, tert-butoxy, phenoxy, and the like; a carboxylate group such as acetate, benzoate and the like; and a sulfonate group such as mesylate, tosylate and the like. Specific examples of the neutral ligand that

can be coordinated with a lone electron pair include organophosphorous compounds such as trimethylphosphine, triethylphosphine, triphenylphosphine, diphenylmethylphosphine and the like; or ethers such as tetrahydrofuran, diethyl ether, dioxane, 1,2-dimethoxyethane and the like. j is an integer from 1 to 4, and when j is 2 or more, Q's may be each the same or different from each other.

[0023]

10 In the following, specific examples of the Group 4 transition metal compound represented by the above general formula [1] are shown. However, the scope of the invention is by no means limited to these examples.

[0024]

butylfluorenyl)zirconium dichloride, di(p-n-
butylphenyl)methylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl)zirconium dichloride, di(p-n-
butylphenyl)methylene(cyclopentadienyl) (2,7-
5 dimethylfluorenyl)zirconium dichloride, di(p-n-
butylphenyl)methylene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl)zirconium dichloride, di(m-
tolyl)methylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl)zirconium dichloride, di(m-
10 tolyl)methylene(cyclopentadienyl) (2,7-
dimethylfluorenyl)zirconium dichloride, di(m-
tolyl)methylene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl)zirconium dichloride, di(p-
tolyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzo
15 fluorenyl)zirconium dichloride, (p-
tolyl)(phenyl)methylene(cyclopentadienyl) (cyclopentadienyl) (c-
octamethyloctahydrodibenzofluorenyl)zirconium dichloride,
di(p-
isopropylphenyl)methylene(cyclopentadienyl) (cyclopentadienyl
20) (octamethyloctahydrodibenzofluorenyl)zirconium dichloride,
di(p-tert-
butylphenyl)methylene(cyclopentadienyl) (cyclopentadienyl) (oc-
tamethyloctahydrodibenzofluorenyl)zirconium dichloride,
di(p-
25 tolyl)methylene(cyclopentadienyl) (cyclopentadienyl) (octameth-

yloctahydrodibenzofluorenyl) zirconium dimethyl, (p-tolyl) (phenyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, di(p-isopropylphenyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, di(p-
5 tolyl)methylene(cyclopentadienyl) (2,7-di-tert-butylphenyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, di(p-tolyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dimethyl, (p-
10 tolyl) (phenyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, di(p-isopropylphenyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, di(p-tert-butylphenyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, di(p-
15 tolyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dimethyl, (p-tert-butylphenyl) (phenyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, (p-tert-
20 butylphenyl) (phenyl)methylene(cyclopentadienyl) (2,7-dimethylfluorenyl) zirconium dichloride, (p-tert-butylphenyl) (phenyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, (p-n-
25 ethylphenyl) (phenyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, (p-n-

ethylphenyl) (phenyl)methylene(cyclopentadienyl) (2,7-dimethylfluorenyl) zirconium dichloride, (p-n-ethylphenyl) (phenyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, (4-5 biphenyl) (phenyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, (4-5 biphenyl) (phenyl)methylene(cyclopentadienyl) (2,7-dimethylfluorenyl) zirconium dichloride, (4-5 biphenyl) (phenyl)methylene(cyclopentadienyl) (3,6-di-tert-10 butylfluorenyl) zirconium dichloride, di(4-5 biphenyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, di(4-5 biphenyl)methylene(cyclopentadienyl) (2,7-dimethylfluorenyl) zirconium dichloride, di(4-15 5 biphenyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, cyclopentylidene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, cyclohexylidene(cyclopentadienyl) (2,7-di-tert-20 butylfluorenyl) zirconium dichloride, adamantlylidene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, cyclopentylidene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, 25 cyclohexylidene(cyclopentadienyl) (3,6-di-tert-

butylfluorenyl) zirconium dichloride,
adamantylidene(cyclopentadienyl) (3,6-di-tert-
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cyclopentylidene(cyclopentadienyl) (2,7-di-tert-
5 butylfluorenyl) hafnium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) hafnium dichloride,
adamantylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) hafnium dichloride,
10 cyclopentylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) titanium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) titanium dichloride,
adamantylidene(cyclopentadienyl) (2,7-di-tert-
15 butylfluorenyl) titanium dichloride,
cyclopropylidene(cyclopentadienyl) (3,6-dimethyl-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3,6-dimethyl-
fluorenyl) zirconium dichloride,
20 cyclopentylidene(cyclopentadienyl) (3,6-dimethyl-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3,6-dimethyl-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3,6-dimethyl-
25 fluorenyl) zirconium dichloride,

cyclopropylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) zirconium dichloride,
5 cyclopentylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3, 6-di-tert-
10 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (3, 6-dicumyl-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3, 6-dicumyl-
fluorenyl) zirconium dichloride,
15 cyclopentylidene(cyclopentadienyl) (3, 6-dicumyl-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3, 6-dicumyl-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3, 6-dicumyl-
20 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (3, 6-di(trimethylsilyl)-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3, 6-di(trimethylsilyl)-
fluorenyl) zirconium dichloride,
25 cyclopentylidene(cyclopentadienyl) (3, 6-di(trimethylsilyl)-

fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3, 6-di(trimethylsilyl)-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3, 6-di(trimethylsilyl)-
5 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (3, 6-diphenyl-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3, 6-diphenyl-
fluorenyl) zirconium dichloride,
10 cyclopentylidene(cyclopentadienyl) (3, 6-diphenyl-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3, 6-diphenyl-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3, 6-diphenyl-
15 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (3, 6-dibenzyl-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3, 6-dibenzyl-
fluorenyl) zirconium dichloride,
20 cyclopentylidene(cyclopentadienyl) (3, 6-dibenzyl-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3, 6-dibenzyl-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3, 6-dibenzyl-
25 fluorenyl) zirconium dichloride,

cyclopropylidene(cyclopentadienyl) (3,6-difluoro-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3,6-difluoro-
fluorenyl) zirconium dichloride,
5 cyclopentylidene(cyclopentadienyl) (3,6-difluoro-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3,6-difluoro-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3,6-difluoro-
10 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (3,6-dibromo-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (3,6-dibromo-
fluorenyl) zirconium dichloride,
15 cyclopentylidene(cyclopentadienyl) (3,6-dibromo-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3,6-dibromo-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (3,6-dibromo-
20 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (3,6-di-tert-
fluorenyl) zirconium dibromide,
cyclobutylidene(cyclopentadienyl) (3,6-di-tert-
fluorenyl) zirconium dibromide,
25 cyclopentylidene(cyclopentadienyl) (3,6-di-tert-

fluorenyl) zirconium dibromide,
cyclohexylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) zirconium dibromide,
cycloheptylidene(cyclopentadienyl) (3, 6-di-tert-
5 fluorenyl) zirconium dibromide,
cyclopropylidene(cyclopentadienyl) (3, 6-dimethyl-
fluorenyl) zirconium dimethyl,
cyclobutylidene(cyclopentadienyl) (3, 6-dimethyl-
fluorenyl) zirconium dimethyl,
10 cyclopentylidene(cyclopentadienyl) (3, 6-dimethyl-
fluorenyl) zirconium dimethyl,
cyclohexylidene(cyclopentadienyl) (3, 6-dimethyl-
fluorenyl) zirconium dimethyl,
cycloheptylidene(cyclopentadienyl) (3, 6-dimethyl-
15 fluorenyl) zirconium dimethyl,
cyclopropylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) hafnium dichloride,
cyclobutylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) hafnium dichloride,
20 cyclopentylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) hafnium dichloride,
cyclohexylidene(cyclopentadienyl) (3, 6-di-tert-
fluorenyl) hafnium dichloride,
cycloheptylidene(cyclopentadienyl) (3, 6-di-tert-
25 fluorenyl) titanium dichloride,

cyclopropylidene(cyclopentadienyl)(3,6-di-tert-fluorenyl)titanium dichloride,
cyclobutylidene(cyclopentadienyl)(3,6-di-tert-fluorenyl)titanium dichloride,
5 cyclopentylidene(cyclopentadienyl)(3,6-di-tert-fluorenyl)titanium dichloride,
cyclohexylidene(cyclopentadienyl)(3,6-di-tert-fluorenyl)titanium dichloride,
cycloheptylidene(cyclopentadienyl)(3,6-di-tert-
10 fluorenyl)titanium dichloride,
cyclopropylidene(cyclopentadienyl)(2,7-dimethyl-fluorenyl)zirconium dichloride,
cyclobutylidene(cyclopentadienyl)(2,7-dimethyl-fluorenyl)zirconium dichloride,
15 cyclopentylidene(cyclopentadienyl)(2,7-dimethyl-fluorenyl)zirconium dichloride,
cyclohexylidene(cyclopentadienyl)(2,7-dimethyl-fluorenyl)zirconium dichloride,
cycloheptylidene(cyclopentadienyl)(2,7-dimethyl-
20 fluorenyl)zirconium dichloride,
cyclopropylidene(cyclopentadienyl)(2,7-di-tert-fluorenyl)zirconium dichloride,
cyclobutylidene(cyclopentadienyl)(2,7-di-tert-
fluorenyl)zirconium dichloride,
25 cyclopentylidene(cyclopentadienyl)(2,7-di-tert-

fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-di-tert-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-di-tert-
5 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (2,7-dicumyl-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (2,7-dicumyl-
fluorenyl) zirconium dichloride,
10 cyclopentylidene(cyclopentadienyl) (2,7-dicumyl-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-dicumyl-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-dicumyl-
15 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (2,7-di(trimethylsilyl)-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (2,7-di(trimethylsilyl)-
fluorenyl) zirconium dichloride,
20 cyclopentylidene(cyclopentadienyl) (2,7-di(trimethylsilyl)-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-di(trimethylsilyl)-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-di(trimethylsilyl)-
25 fluorenyl) zirconium dichloride,

cyclopropylidene(cyclopentadienyl) (2,7-diphenyl-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (2,7-diphenyl-
fluorenyl) zirconium dichloride,
5 cyclopentylidene(cyclopentadienyl) (2,7-diphenyl-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-diphenyl-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-diphenyl-
10 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (2,7-dibenzyl-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (2,7-dibenzyl-
fluorenyl) zirconium dichloride,
15 cyclopentylidene(cyclopentadienyl) (2,7-dibenzyl-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-dibenzyl-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-dibenzyl-
20 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (2,7-difluoro-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (2,7-difluoro-
fluorenyl) zirconium dichloride,
25 cyclopentylidene(cyclopentadienyl) (2,7-difluoro-

fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-difluoro-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-difluoro-
5 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (2,7-dibromo-
fluorenyl) zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (2,7-dibromo-
fluorenyl) zirconium dichloride,
10 cyclopentylidene(cyclopentadienyl) (2,7-dibromo-
fluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-dibromo-
fluorenyl) zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-dibromo-
15 fluorenyl) zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (2,7-di-tert-
fluorenyl) zirconium dibromide,
cyclobutylidene(cyclopentadienyl) (2,7-di-tert-
fluorenyl) zirconium dibromide,
20 cyclopentylidene(cyclopentadienyl) (2,7-di-tert-
fluorenyl) zirconium dibromide,
cyclohexylidene(cyclopentadienyl) (2,7-di-tert-
fluorenyl) zirconium dibromide,
cycloheptylidene(cyclopentadienyl) (2,7-di-tert-
25 fluorenyl) zirconium dibromide,

cyclopropylidene(cyclopentadienyl)(2,7-dimethyl-
fluorenyl)zirconium dimethyl,
cyclobutylidene(cyclopentadienyl)(2,7-dimethyl-
fluorenyl)zirconium dimethyl,
5 cyclopentylidene(cyclopentadienyl)(2,7-dimethyl-
fluorenyl)zirconium dimethyl,
cyclohexylidene(cyclopentadienyl)(2,7-dimethyl-
fluorenyl)zirconium dimethyl,
cycloheptylidene(cyclopentadienyl)(2,7-dimethyl-
10 fluorenyl)zirconium dimethyl,
cyclopropylidene(cyclopentadienyl)(2,7-di-tert-
fluorenyl)hafnium dichloride,
cyclobutylidene(cyclopentadienyl)(2,7-di-tert-
fluorenyl)hafnium dichloride,
15 cyclopentylidene(cyclopentadienyl)(2,7-di-tert-
fluorenyl)hafnium dichloride,
cyclohexylidene(cyclopentadienyl)(2,7-di-tert-
fluorenyl)hafnium dichloride,
cycloheptylidene(cyclopentadienyl)(2,7-di-tert-
20 fluorenyl)titanium dichloride,
cyclopropylidene(cyclopentadienyl)(2,7-di-tert-
fluorenyl)titanium dichloride,
cyclobutylidene(cyclopentadienyl)(2,7-di-tert-
fluorenyl)titanium dichloride,
25 cyclopentylidene(cyclopentadienyl)(2,7-di-tert-

fluorenyl)titanium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-di-tert-
fluorenyl)titanium dichloride,
cycloheptylidene(cyclopentadienyl) (2,7-di-tert-
5 fluorenyl)titanium dichloride,
cyclopropylidene(cyclopentadienyl) (octamethyloctahydrodibenz
o fluorenyl)zirconium dichloride,
cyclobutylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl)zirconium dichloride,
10 cyclopentylidene(cyclopentadienyl) (octamethyloctahydrodibenz
o fluorenyl)zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl)zirconium dichloride,
cycloheptylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
15 fluorenyl)zirconium dichloride,
cyclopropylidene(cyclopentadienyl) (octamethyloctahydrodibenz
o fluorenyl)zirconium dibromide,
cyclobutylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl)zirconium dibromide,
20 cyclopentylidene(cyclopentadienyl) (octamethyloctahydrodibenz
o fluorenyl)zirconium dibromide,
cyclohexylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl)zirconium dibromide,
cycloheptylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
25 fluorenyl)zirconium dibromide,

cyclopropylidene(cyclopentadienyl) (octamethyloctahydrodibenz
ofluorenyl) zirconium dimethyl,
cyclobutylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl) zirconium dimethyl,
5 cyclopentylidene(cyclopentadienyl) (octamethyloctahydrodibenz
ofluorenyl) zirconium dimethyl,
cyclohexylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl) zirconium dimethyl,
cycloheptylidene(cyclopentadienyl) (octamethyloctahydrodibenz
10 ofluorenyl) zirconium dimethyl,
cyclopropylidene(cyclopentadienyl) (octamethyloctahydrodibenz
ofluorenyl) hafnium dichloride,
cyclobutylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl) hafnium dichloride,
15 cyclopentylidene(cyclopentadienyl) (octamethyloctahydrodibenz
ofluorenyl) hafnium dichloride,
cyclohexylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl) hafnium dichloride,
cycloheptylidene(cyclopentadienyl) (octamethyloctahydrodibenz
20 ofluorenyl) titanium dichloride,
cyclopropylidene(cyclopentadienyl) (octamethyloctahydrodibenz
ofluorenyl) titanium dichloride,
cyclobutylidene(cyclopentadienyl) (octamethyloctahydrodibenzo
fluorenyl) titanium dichloride,
25 cyclopentylidene(cyclopentadienyl) (octamethyloctahydrodibenz

ofluorenyl)titanium dichloride,
cyclohexylidene(cyclopentadienyl)(octamethyloctahydrodibenzo
fluorenyl)titanium dichloride,
cycloheptylidene(cyclopentadienyl)(octamethyloctahydrodibenz
5 ofluorenyl)titanium dichloride, di-n-butylmethylen
(cyclopentadienyl)(fluorenyl)zirconium dichloride, di-n-
butylmethylen(cyclopentadienyl)(2,7-di-tert-
butylfluorenyl)zirconium dichloride, di-n-
butylmethylen(cyclopentadienyl)(3,6-di-tert-
10 butylfluorenyl)zirconium dichloride, di-n-
butylmethylen(cyclopentadienyl)(octamethyloctahydrodibenzof
luorenyl)zirconium dichloride, di-n-
butylmethylen(cyclopentadienyl)(benzofluorenyl)zirconium
dichloride, di-n-
15 butylmethylen(cyclopentadienyl)(dibenzofluorenyl)zirconium
dichloride, di-n-
butylmethylen(cyclopentadienyl)(octahydrodibenzofluorenyl)
zirconium dichloride, di-n-
butylmethylen(cyclopentadienyl)(octamethyltetrahydroadicyclo
20 pentafluorenyl)zirconium dichloride,
diisobutylmethylen(cyclopentadienyl)(2,7-di-tert-
butylfluorenyl)zirconium dichloride,
diisobutylmethylen(cyclopentadienyl)(3,6-di-tert-
butylfluorenyl)zirconium dichloride,
25 diisobutylmethylen(cyclopentadienyl)(octamethyloctahydrodib

enzo fluorenyl) zirconium dichloride,
diisobutylmethylene(cyclopentadienyl)(benzofluorenyl) zirconium dichloride,
diisobutylmethylene(cyclopentadienyl)(dibenzofluorenyl) zirconium dichloride,
diisobutylmethylene(cyclopentadienyl)(octahydro dibenzofluorenyl) zirconium dichloride,
diisobutylmethylene(cyclopentadienyl)(octamethyltetrahydrodicyclopentafluorenyl) zirconium dichloride,
dibenzylmethylene(cyclopentadienyl)(2,7-di-tert-butylfluorenyl) zirconium dichloride,
dibenzylmethylene(cyclopentadienyl)(3,6-di-tert-butylfluorenyl) zirconium dichloride,
dibenzylmethylene(cyclopentadienyl)(octamethyloctahydrodibenzo fluorenyl) zirconium dichloride,
dibenzylmethylene(cyclopentadienyl)(benzofluorenyl) zirconium dichloride,
dibenzylmethylene(cyclopentadienyl)(dibenzofluorenyl) zirconium dichloride,
dibenzylmethylene(cyclopentadienyl)(octahydro dibenzofluorenly) zirconium dichloride,
dibenzylmethylene(cyclopentadienyl)(octamethyltetrahydrodicyclopentafluorenyl) zirconium dichloride,
diphenethylmethylene(cyclopentadienyl)(2,7-di-tert-butylfluorenyl) zirconium dichloride,

diphenethylmethlene(cyclopentadienyl) (3,6-di-tert-
butylfluorenlyl) zirconium dichloride,
diphenethylmethlene(cyclopentadienyl) (octamethyloctahydrodi
benzofluorenlyl) zirconium dichloride,
5 diphenethylmethlene(cyclopentadienyl) (benzofluorenlyl) zircon
ium dichloride,
diphenethylmethlene(cyclopentadienyl) (dibenzofluorenlyl) zirc
onium dichloride,
diphenethylmethlene(cyclopentadienyl) (octahydrodibenzofluor
10 enyl) zirconium dichloride,
diphenethylmethlene(cyclopentadienyl) (octamethyltetrahydron
icyclopentafluorenlyl) zirconium dichloride,
di(benzhydryl)methylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenlyl) zirconium dichloride,
15 di(benzhydryl)methylene(cyclopentadienyl) (3,6-di-tert-
butylfluorenlyl) zirconium dichloride,
di(benzhydryl)methylene(cyclopentadienyl) (octamethyloctahydr
odibenzofluorenlyl) zirconium dichloride,
di(benzhydryl)methylene(cyclopentadienyl) (benzofluorenlyl) zir
20 conium dichloride,
di(benzhydryl)methylene(cyclopentadienyl) (dibenzofluorenlyl) z
irconium dichloride,
di(benzhydryl)methylene(cyclopentadienyl) (octahydrodibenzoflu
orenlyl) zirconium dichloride,
25 di(benzhydryl)methylene(cyclopentadienyl) (octamethyltetrahyd

rodi(cyclopentafluorenyl)zirconium dichloride,
di(cumyl)methylene (cyclopentadienyl) (fluorenyl)zirconium
dichloride, di(cumyl)methylene(cyclopentadienyl) (2,7-di-
tert-butylfluorenyl)zirconium dichloride,
5 di(cumyl)methylene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl)zirconium dichloride,
di(cumyl)methylene(cyclopentadienyl) (octamethyloctahydrodibe-
nzofluorenyl)zirconium dichloride,
di(cumyl)methylene(cyclopentadienyl) (benzofluorenyl)zirconiu-
10 m dichloride,
di(cumyl)methylene(cyclopentadienyl) (dibenzofluorenyl)zircon-
ium dichloride,
di(cumyl)methylene(cyclopentadienyl) (octahydrodibenzofluoren-
yl)zirconium dichloride,
15 di(cumyl)methylene(cyclopentadienyl) (octamethyltetrahydrodic-
yclopentafluorenyl)zirconium dichloride, di(1-phenyl-
ethyl)methylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl)zirconium dichloride, di(1-phenyl-
ethyl)methylene(cyclopentadienyl) (3,6-di-tert-
20 butylfluorenyl)zirconium dichloride, di(1-phenyl-
ethyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzo-
fluorenyl)zirconium dichloride, di(1-phenyl-
ethyl)methylene(cyclopentadienyl) (benzofluorenyl)zirconium
dichloride, di(1-phenyl-
25 ethyl)methylene(cyclopentadienyl) (dibenzofluorenyl)zirconium

dichloride, di(1-phenyl-
ethyl)methylene(cyclopentadienyl) (octahydrodibenzofluorenyl)
zirconium dichloride, di(1-phenyl-
ethyl)methylene(cyclopentadienyl) (octamethyltetrahydrodicycl
5 opentafluorenyl) zirconium dichloride,
di(cyclohexylmethyl)methylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
di(cyclohexylmethyl)methylene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl) zirconium dichloride,
10 di(cyclohexylmethyl)methylene(cyclopentadienyl) (octamethyloc-
tahydrodibenzofluorenyl) zirconium dichloride,
di(cyclohexylmethyl)methylene(cyclopentadienyl) (benzofluoren-
yl) zirconium dichloride,
di(cyclohexylmethyl)methylene(cyclopentadienyl) (dibenzofluor-
15 enyl) zirconium dichloride,
di(cyclohexylmethyl)methylene(cyclopentadienyl) (octahydrodib-
enzofluorenyl) zirconium dichloride,
di(cyclohexylmethyl)methylene(cyclopentadienyl) (octamethylte-
trahydrodicyclopentafluorenyl) zirconium dichloride, di(1-
20 cyclohexyl-ethyl)methylene
(cyclopentadienyl) (fluorenyl) zirconium dichloride, di(1-
cyclohexyl-ethyl)methylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride, di(1-cyclohexyl-
ethyl)methylene(cyclopentadienyl) (3,6-di-tert-
25 butylfluorenyl) zirconium dichloride, di(1-cyclohexyl-

ethyl)methylene(cyclopentadienyl)(octamethyloctahydrodibenzo
fluorenyl)zirconium dichloride, di(1-cyclohexyl-
ethyl)methylene(cyclopentadienyl)(benzofluorenyl)zirconium
dichloride, di(1-cyclohexyl-
5 ethyl)methylene(cyclopentadienyl)(dibenzofluorenyl)zirconium
dichloride, di(1-cyclohexyl-
ethyl)methylene(cyclopentadienyl)(octahydrodibenzofluorenyl)
zirconium dichloride, di(1-cyclohexyl-
ethyl)methylene(cyclopentadienyl)(octamethyltetrahydroadicycl
10 opentafluorenyl)zirconium dichloride,
di(cyclopentylmethyl)methylene(cyclopentadienyl)(2,7-di-
tert-butylfluorenyl)zirconium dichloride,
di(cyclopentylmethyl)methylene(cyclopentadienyl)(3,6-di-
tert-butylfluorenyl)zirconium dichloride,
15 di(cyclopentylmethyl)methylene(cyclopentadienyl)(octamethylo-
ctahydrodibenzofluorenyl)zirconium dichloride,
di(cyclopentylmethyl)methylene(cyclopentadienyl)(benzofluore-
nyl)zirconium dichloride,
di(cyclopentylmethyl)methylene(cyclopentadienyl)(dibenzofluo-
20 renyl)zirconium dichloride,
di(cyclopentylmethyl)methylene(cyclopentadienyl)(octahydrodi-
benzofluorenyl)zirconium dichloride,
di(cyclopentylmethyl)methylene(cyclopentadienyl)(octamethyltetrahydroadicyclo-
25 pentafluorenyl)zirconium dichloride, di(1-
cyclopentyl-ethyl)methylene

(cyclopentadienyl) (fluorenyl) zirconium dichloride, di(1-cyclopentyl-ethyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, di(1-cyclopentyl-ethyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, di(1-cyclopentyl-ethyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzo fluorenyl) zirconium dichloride, di(1-cyclopentyl-ethyl)methylene(cyclopentadienyl) (benzofluorenyl) zirconium dichloride, di(1-cyclopentyl-ethyl)methylene(cyclopentadienyl) (dibenzofluorenyl) zirconium dichloride, di(1-cyclopentyl-ethyl)methylene(cyclopentadienyl) (octahydrodibenzofluorenyl) zirconium dichloride, di(1-cyclopentyl-ethyl)methylene(cyclopentadienyl) (octamethyltetrahydrodicyclo pentafluorenyl) zirconium dichloride,
di(naphthylmethyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride,
di(naphthylmethyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride,
di(naphthylmethyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzo fluorenyl) zirconium dichloride,
di(naphthylmethyl)methylene(cyclopentadienyl) (benzofluorenyl) zirconium dichloride,
di(naphthylmethyl)methylene(cyclopentadienyl) (dibenzofluorenyl) zirconium dichloride,

di(naphthylmethyl)methylene(cyclopentadienyl)(octahydrodibenzofluorenyl)zirconium dichloride,

di(naphthylmethyl)methylene(cyclopentadienyl)(octamethyltetrahydrodicyclopentafluorenyl)zirconium dichloride,

5 di(biphenylmethyl)methylene(cyclopentadienyl)(fluorenyl)zirconium dichloride,

di(biphenylmethyl)methylene(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride,

di(biphenylmethyl)methylene(cyclopentadienyl)(3,6-di-tert-

10 butylfluorenyl)zirconium dichloride,

di(biphenylmethyl)methylene(cyclopentadienyl)(octamethyloctahydrodibenzofluorenyl)zirconium dichloride,

di(biphenylmethyl)methylene(cyclopentadienyl)(benzofluorenyl)zirconium dichloride,

15 di(biphenylmethyl)methylene(cyclopentadienyl)(dibenzofluorenyl)zirconium dichloride,

di(biphenylmethyl)methylene(cyclopentadienyl)(octahydrodibenzofluorenyl)zirconium dichloride,

di(biphenylmethyl)methylene(cyclopentadienyl)(octamethyltetra-

20 ahydrodicyclopentafluorenyl)zirconium dichloride,

(benzyl)(phenethyl)methylene(cyclopentadienyl)(fluorenyl)zirconium dichloride,

(benzyl)(phenethyl)methylene(cyclopentadienyl)(2,7-di-tert-butylfluorenyl)zirconium dichloride,

25 (benzyl)(phenethyl)methylene(cyclopentadienyl)(3,6-di-tert-

butylfluorenyl) zirconium dichloride,
(benzyl) (phenethyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzofluorenyl) zirconium dichloride, (benzyl) (n-butyl)methylene (cyclopentadienyl) (fluorenyl) zirconium
5 dichloride, (benzyl) (n-butyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride, (benzyl) (n-butyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride, (benzyl) (n-
10 butyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzo fluorenyl) zirconium dichloride,
(benzyl) (cumyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride,
(benzyl) (cumyl)methylene(cyclopentadienyl) (3,6-di-tert-
15 butylfluorenyl) zirconium dichloride,
(benzyl) (cumyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzofluorenyl) zirconium dichloride,
(benzyl) (cyclohexylmethyl)methylene(cyclopentadienyl) (2,7-di-tert-butylfluorenyl) zirconium dichloride,
20 (benzyl) (cyclohexylmethyl)methylene(cyclopentadienyl) (3,6-di-tert-butylfluorenyl) zirconium dichloride,
(benzyl) (cyclohexylmethyl)methylene(cyclopentadienyl) (octamethyloctahydrodibenzofluorenyl) zirconium dichloride,
dibenzylmethlene(cyclopentadienyl) (2,7-di-tert-
25 butylfluorenyl) titanium dichloride,

dibenzylmethlene(cyclopentadienyl)(3,6-di-tert-
butylfluorenyl)titanium dichloride,
dibenzylmethlene(cyclopentadienyl)(octamethyloctahydrodiben
zofluorenyl)titanium dichloride,
5 dibenzylmethlene(cyclopentadienyl)(2,7-di-tert-
butylfluorenyl)hafnium dichloride,
dibenzylmethlene(cyclopentadienyl)(3,6-di-tert-
butylfluorenyl)hafnium dichloride,
dibenzylmethlene(cyclopentadienyl)(octamethyloctahydrodiben
10 zofluorenyl)hafnium dichloride,
dibenzylmethlene(cyclopentadienyl)(2,7-di-tert-
butylfluorenyl)zirconium dibromide,
dibenzylmethlene(cyclopentadienyl)(3,6-di-tert-
butylfluorenyl)zirconium dibromide,
15 dibenzylmethlene(cyclopentadienyl)(octamethyloctahydrodiben
zofluorenyl)zirconium dibromide,
dibenzylmethlene(cyclopentadienyl)(2,7-di-tert-
butylfluorenyl)zirconium dimethyl,
dibenzylmethlene(cyclopentadienyl)(3,6-di-tert-
20 butylfluorenyl)zirconium dimethyl,
dibenzylmethlene(cyclopentadienyl)(octamethyloctahydrodiben
zofluorenyl)zirconium dimethyl,
dimethylmethlene(cyclopentadienyl)(2,7-di-tert-
butylfluorenyl)zirconium dimethyl,
25 dimethylmethlene(cyclopentadienyl)(3,6-di-tert-

butylfluorenyl) zirconium dimethyl,
dimethylmethylenecyclopentadienyl (octamethyloctahydrobenzo fluorenyl) zirconium dimethyl,
dimethylmethylenecyclopentadienyl (benzofluorenyl) zirconium
5 dimethyl,
dimethylmethylenecyclopentadienyl (dibenzofluorenyl) zirconium dimethyl,
dimethylmethylenecyclopentadienyl (octahydronaphthalen-1-yl) zirconium dimethyl,
10 dimethylmethylenecyclopentadienyl (octamethyltetrahydronaphthalen-1-yl) zirconium dimethyl,
dimethylmethylenecyclopentadienyl (2,7-di-tert-butylfluorenyl) zirconium dichloride,
dimethylmethylenecyclopentadienyl (3,6-di-tert-
15 butylfluorenyl) zirconium dichloride,
dimethylmethylenecyclopentadienyl (benzofluorenyl) zirconium dichloride,
dimethylmethylenecyclopentadienyl (benzofluorenyl) zirconium
20 dichloride,
dimethylmethylenecyclopentadienyl (dibenzofluorenyl) zirconium dichloride,
dimethylmethylenecyclopentadienyl (octahydronaphthalen-1-yl) zirconium dichloride,
dimethylmethylenecyclopentadienyl (octamethyltetrahydronaphthalen-1-yl) zirconium dichloride,
25 clopentafluorenyl) zirconium dichloride,

dimethylsilylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
dimethylsilylene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl) zirconium dichloride,
5 dimethylsilylene(cyclopentadienyl) (octamethyloctahydrodibenz
ofluorenyl) zirconium dichloride,
dimethylsilylene(cyclopentadienyl) (benzofluorenyl) zirconium
dichloride,
dimethylsilylene(cyclopentadienyl) (dibenzofluorenyl) zirconiu
10 m dichloride,
dimethylsilylene(cyclopentadienyl) (octahydrodibenzofluorenyl
) zirconium dichloride,
dimethylsilylene(cyclopentadienyl) (octamethyltetrahydronicyc
lopentafluorenyl) zirconium dichloride,
15 dimethylsilylene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dimethyl,
dimethylsilylene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl) zirconium dimethyl,
dimethylsilylene(cyclopentadienyl) (octamethyloctahydrodibenz
20 ofluorenyl) zirconium dimethyl,
dimethylsilylene(cyclopentadienyl) (benzofluorenyl) zirconium
dimethyl,
dimethylsilylene(cyclopentadienyl) (dibenzofluorenyl) zirconiu
m dimethyl,
25 dimethylsilylene(cyclopentadienyl) (octahydrodibenzofluorenyl

) zirconium dimethyl,
dimethylsilylene(cyclopentadienyl) (octamethyltetrahydrocyclopendafluorenyl) zirconium dimethyl,
cyclopentylidene(cyclopentadienyl) (2,7-di-tert-
5 butylfluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
adamantylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
10 monophenylmonomethylmethylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
dimethylmethylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
diphenylmethylenecyclopentadienyl) (2,7-di-tert-
15 butylfluorenyl) zirconium dichloride, di(p-
tolyl)methylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
diethylmethylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl) zirconium dichloride,
20 cyclopentylidene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl) zirconium dichloride,
cyclohexylidene(cyclopentadienyl) (3,6-di-tert-
butylfluorenyl) zirconium dichloride,
adamantylidene(cyclopentadienyl) (3,6-di-tert-
25 butylfluorenyl) zirconium dichloride,

monophenylmonomethylmethylenecyclopentadienyl) (3, 6-di-tert-
butylfluorenyl) zirconium dichloride,
dimethylmethylenecyclopentadienyl) (3, 6-di-tert-
butylfluorenyl) zirconium dichloride,
5 diphenylmethylenecyclopentadienyl) (3, 6-di-tert-
butylfluorenyl) zirconium dichloride, di(p-
tolyl)methylenecyclopentadienyl) (3, 6-di-tert-
butylfluorenyl) zirconium dichloride,
diethylmethylenecyclopentadienyl) (3, 6-di-tert-
10 butylfluorenyl) zirconium dichloride,
cyclopentylidene(cyclopentadienyl) (2, 7-di-tert-
butylfluorenyl) hafnium dichloride,
cyclohexylidene(cyclopentadienyl) (2, 7-di-tert-
butylfluorenyl) hafnium dichloride,
15 adamantlylidene(cyclopentadienyl) (2, 7-di-tert-
butylfluorenyl) hafnium dichloride,
monophenylmonomethylmethylenecyclopentadienyl) (2, 7-di-tert-
butylfluorenyl) hafnium dichloride,
dimethylmethylenecyclopentadienyl) (2, 7-di-tert-
20 butylfluorenyl) hafnium dichloride,
diphenylmethylenecyclopentadienyl) (2, 7-di-tert-
butylfluorenyl) hafnium dichloride, di(p-
tolyl)methylenecyclopentadienyl) (2, 7-di-tert-
butylfluorenyl) hafnium dichloride,
25 diethylmethylenecyclopentadienyl) (2, 7-di-tert-

butylfluorenyl)hafnium dichloride,
cyclopentylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl)titanium dichloride,
cyclohexylidene(cyclopentadienyl) (2,7-di-tert-
5 butylfluorenyl)titanium dichloride,
adamantylidene(cyclopentadienyl) (2,7-di-tert-
butylfluorenyl)titanium dichloride,
monophenylmonomethylmethylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl)titanium dichloride,
10 dimethylmethylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl)titanium dichloride,
diphenylmethylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl)titanium dichloride, di(p-
tolyl)methylenecyclopentadienyl) (2,7-di-tert-
15 butylfluorenyl)titanium dichloride,
diethylmethylenecyclopentadienyl) (2,7-di-tert-
butylfluorenyl)titanium dichloride. Further, in the above
compounds, the compounds in which "cyclopentadienyl" is
replaced with "(3-tert-butyl-5-methyl-cyclopentadienyl)",
20 "(3,5-dimethyl-cyclopentadienyl)", or the like are also
included. The metallocene compounds of the invention are
not limited to above exemplified compounds, but include all
the compounds satisfying the requirements defined in claims.

[0025]

25 Preferable embodiments for providing the bridged

metallocene compound as catalyst for olefin polymerization

Next, preferred embodiments for providing the bridged metallocene compound used as a catalyst for the olefin polymerization method of the invention will be explained.

5 [0026]

When the bridged metallocene compound of the invention is used as a catalyst for olefin polymerization, the catalyst components consist of:

(A) a metallocene compound represented by the above
10 general formula [1], and
(B) at least compound selected from (B-1) an organometallic compound, (B-2) an organoaluminum oxy compound, and (B-3) a compound which reacts with the bridged metallocene compound (A) to form an ion pair.

15 [0027]

Hereinafter, the respective components will be described in detail.

[0028]

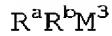
(B-1) Organometallic compound

20 As the organometallic compound (B-1) used in the invention, specifically, the following organometallic compounds are employed.

[0029]

Dialkyl compound of a metal belonging to Group 2 or a
25 Group 12 of the Periodic Table, represented by the general

formula:



(wherein R^a and R^b may be the same or different from each other, and each represent a hydrocarbon group having 1 to 15 carbon atoms, and preferably 1 to 4 carbon atoms. M^3 is Mg, 5 Zn or Cd.) Further, these organometallic compounds (B-1) may be used alone or in combination of two or more species.

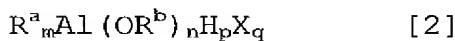
[0030]

(B-2) Organoaluminum compound

10 As the organoaluminum compound (B-2) which constitutes the catalyst for olefin polymerization, mention may be made of, for example, the organoaluminum compound represented by the following general formula [2], an alkylated complex containing a Group 1 metal and aluminum, represented by the 15 following general formula [3], an organoaluminum oxy compound and the like.

[0031]

Organoaluminum compounds represented by

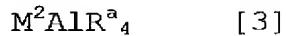


20 (wherein R^a and R^b may be the same or different from each other, and each represent a hydrocarbon group having 1 to 15 carbon atoms, and preferably 1 to 4 carbon atoms. X represents a halogen atom; m , n , p , and q are numbers satisfying the conditions: $0 < m \leq 3$, $0 \leq n < 3$, $0 \leq p < 3$, 25 and $0 \leq q < 3$, while $m + n + p + q = 3$.) Specific examples

of such compounds include trimethylaluminum,
triethylaluminum, triisobutylaluminum, diisobutylaluminum
hydride and the like.

[0032]

5 Alkylated complexes containing a Group 1 metal and
aluminum, represented by the general formula [3]:



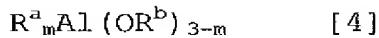
(wherein M^2 represents Li, Na, or K; and R^a represent a
hydrocarbon group having 1 to 15 carbon atoms, and

10 preferably 1 to 4 carbon atoms). Such compounds are
exemplified by $LiAl(C_2H_5)_4$, $LiAl(C_7H_{15})_4$, and the like.

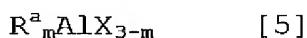
[0033]

Examples of the organoaluminum compound represented by
the above general formula [2] include the compounds
15 represented by following general formula [4], [5], [6] or
[7].

[0034]

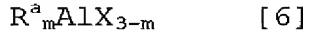


(wherein R^a and R^b may be the same or different from each
20 other each other, and each represent a hydrocarbon group
having 1 to 15 carbon atoms, and preferably 1 to 4 carbon
atoms, and m is the numbers satisfying the conditions: $1.5 \leq m \leq 3.$)

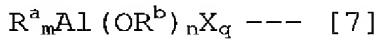


25 (wherein R^a represents a hydrocarbon group having 1 to 15

carbon atoms, and preferably 1 to 4 carbon atoms; X represents a halogen atom; and m is in the range of $0 < m < 3$)



5 (wherein R^a represents a hydrocarbon group having 1 to 15 carbon atoms, and preferably 1 to 4 carbon atoms; X represents a halogen atom; and m is in the range of $2 \leq m < 3$)



10 (wherein R^a and R^b may be the same or different from each other each other, and each represent a hydrocarbon group having 1 to 15 carbon atoms, and preferably 1 to 4 carbon atoms, and m, n, and q are numbers satisfying the conditions: $0 < m \leq 3$, $0 \leq n < 3$, and $0 \leq q < 3$, while $m + n$
15 + q = 3).

Specific examples of the aluminum compound represented by the general formula [4], [5], [6] or [7] include tri-n-alkylaluminum such as trimethylaluminum, triethylaluminum, tri-n-butylaluminum, tripropylaluminum, tripentylaluminum,
20 trihexylaluminum, trioctylaluminum, tridecylaluminum and the like; tri-branched-chain alkylaluminum such as triisopropylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-

methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum, tri-2-ethylhexylaluminum and the like; tricycloalkylaluminum such as tricyclohexylaluminum, tricyclooctylaluminum, and the like; triarylaluminum such as 5 triphenylaluminum, tritolylaluminum, and the like; dialkylaluminum halide such as diisopropylaluminum halide, diisobutylaluminum halide, and the like; alkenylaluminum such as isoprenylaluminum etc. represented by the general formula $(i\text{-C}_4\text{H}_9)_x\text{Al}_y(\text{C}_5\text{H}_{10})_z$ (wherein x, y, and z are positive 10 integers, and z is the numbers satisfying the conditions: $z \leq 2x$); alkylaluminum alkoxide such as isobutylaluminum methoxide, isobutylaluminum ethoxide, isobutylaluminum isopropoxide and the like; dialkylaluminum alkoxide such as dimethylaluminum methoxide, diethylaluminum ethoxide, 15 dibutylaluminum butoxide, and the like; alkylaluminum sesquialkoxide such as ethylaluminum sesquiethoxide, butylaluminum sesquibutoxide, and the like; partially alkoxylated alkylaluminum having mean compositions represented by the general formula $\text{R}^a_{2.5}\text{Al}(\text{OR}^b)_{0.5}$ and the 20 like; alkylaluminum aryloxide such as diethylaluminum phenoxide, diethylaluminum(2,6-di-t-butyl-4-methylphenoxyde), ethylaluminumbis(2,6-di-t-butyl-4-methylphenoxyde), diisobutylaluminum(2,6-di-t-butyl-4-methylphenoxyde), isobutylaluminum bis(2,6-di-t-butyl-4-methylphenoxyde) and 25 the like; dialkylaluminum halide such as dimethylaluminum

chloride, diethylaluminum chloride, dibutylaluminum chloride,
diethylaluminum bromide, diisobutylaluminum chloride, and
the like; alkylaluminum sesquihalide such as ethylaluminum
sesquichloride, butylaluminum sesquichloride, ethylaluminum
sesquibromide, and the like; partially halogenated
alkylaluminum such as alkylaluminum dihalide such as
ethylaluminum dichloride, propylaluminum dichloride,
butylaluminum dibromide and the like; dialkylaluminum
hydride such as diethylaluminum hydride, dibutylaluminum
hydride, and the like; partially hydrogenated alkylaluminum
such as alkylaluminum dihydride such as ethylaluminum
dihydride, propylaluminum dihydride, and the like; and
partially alkoxylated and halogenated alkylaluminum such as
ethylaluminum ethoxychloride, butylaluminum butoxychloride,
ethylaluminum ethoxybromide, and the like.

[0035]

Further, the compounds analogous to those represented
by the above general formula [2] can also be used, and
examples thereof include organoaluminum compounds in which
at least two aluminum compounds are bonded via a nitrogen
atom. Specific examples of such the compounds include
 $(C_2H_5)_2AlN(C_2H_5)Al(C_2H_5)_2$ and the like.

[0036]

The compounds represented by the above general formula
[3] are exemplified by $LiAl(C_2H_5)_4$, $LiAl(C_7H_{15})_4$, and the like.

[0037]

Further, the compound which is formed by the above organoaluminum compound in the polymerization system, for example, a combination of aluminum halide and alkyl lithium,
5 a combination of aluminum halide and alkyl magnesium, or the like can be used.

[0038]

Among these compounds, the organoaluminum compound is preferable.

10 [0039]

The organoaluminum compounds represented by the above general formula [2] or the alkylated complex containing a Group 1 metal and aluminum, represented by the above general formula [3] are used alone or in combination of two or more
15 species.

[0040]

(B-3) Organoaluminum oxy compound

The organoaluminum oxy compound (B-3) used in the invention may be aluminoxane known in the art or the
20 organoaluminum oxy compounds which are insoluble in benzene as exemplified in JP-A No. 2-78687.

[0041]

The aluminoxane known in the art can be obtained, for example, by the following methods, and can be typically
25 obtained as a solution in the hydrocarbon solvent.

(1) A method of adding an organoaluminum compound such as trialkylaluminum to a suspension of a compound having absorbed water or a salt containing water of crystallization, for example, magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate, or cereus chloride hydrate in a hydrocarbon medium, to react the organoaluminum compound with the absorbed water or the water of crystallization.

(2) A method of reacting water, ice or water vapor directly with an organoaluminum compound such as trialkylaluminum in a medium such as benzene, toluene, ethylether, or tetrahydrofuran.

(3) A method of reacting an organoaluminum compound such as trialkylaluminum with an organotin oxide such as dimethyltin oxide, and dibutyltin oxide in a medium such as decane, benzene, or toluene.

[0042]

The above aluminoxane may contain a small amount of the organometallic component. Further, after distilling off the solvent or the unreacted organoaluminum compound from the above recovered aluminoxane solution, the aluminoxane may be redissolved or suspended in a poor solvent of aluminoxane.

[0043]

Specific examples of the organoaluminum compounds used in the preparation of aluminoxane include the same

organoaluminum compounds as those exemplified as the organoaluminum compounds of the above (B-2).

[0044]

Among them, trialkylaluminum and tricycloalkylaluminum
5 are preferable, and trimethylaluminum is particularly preferable.

[0045]

Such organoaluminum compound can be used alone or in combination of two or more species.

10 [0046]

The organoaluminum oxy compound which is insoluble in benzene used in the invention preferably has Al components dissolved in benzene at 60°C by 10% or less, preferably 5% or less, and particularly preferably 2% or less, in terms of 15 Al atom. That is, those compounds are preferably insoluble or hardly soluble in benzene. Such organoaluminum oxy compound (B-3) can be used alone or in combination of two or more species.

[0047]

20 Moreover, aluminoxane produced from trimethylaluminum is referred to as methylaluminoxane, or MAO, which is a particularly frequently used compound.

[0048]

As the solvent used in the preparation of aluminoxane,
25 mention may be made of aromatic hydrocarbons such as benzene,

toluene, xylene, cumene and cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, cyclooctane and

5 methylcyclopentane; petroleum fractions such as gasoline, kerosene and gas oil; and halides of the aforementioned aromatic hydrocarbons, aliphatic hydrocarbons, and alicyclic hydrocarbons, inter alia, chlorinated or brominated hydrocarbon solvents. In addition, mention may be also made

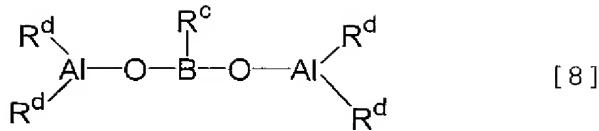
10 of ethers such as ethyl ether and tetrahydrofuran. Among the solvents, particularly preferred are the aromatic hydrocarbons or the aliphatic hydrocarbons.

[0049]

The organoaluminum oxy compound which is insoluble in benzene used in the invention has Al components dissolved in benzene at 60°C by 10% or less, preferably 5% or less, particularly preferably 2% or less, in terms of Al atom. That is, those compounds are insoluble or hardly soluble in benzene.

20 [0050]

As the organoaluminum oxy compounds used in the present invention, mention may be made of the organoaluminum oxy compounds containing boron represented by the following general formula [8].



[0052]

(wherein R^c represents a hydrocarbon group having 1 to 10 carbon atoms. R^d may be the same or different from each other, and represents a hydrogen atom, a halogen atom, or a hydrocarbon group having 1 to 10 carbon atoms.)

The organoaluminum oxy compounds containing boron represented by the above general formula [8] can be produced by reacting alkyl borate represented by the general formula [9] and an organoaluminum compound in an inert solvent, at inert gas atmosphere under the condition of temperature of - 80°C to room temperature and a reaction time of 1 minute to 24 hours.

[0053]

$R^c B(OH)_2 --- [9]$

(wherein R^c has the same meaning as above.)

The specific examples of the alkyl borate represented by the general formula [9], include methyl borate, ethyl borate, isopropyl borate, n-propyl borate, n-butyl borate, isobutyl borate, n-hexyl borate, cyclohexyl borate, phenyl borate, 3,5-difluorophenyl borate, pentafluorophenyl borate, 3,5-bis(trifluoromethyl)phenyl borate and the like. Among these compounds, methyl borate, n-butyl borate, isobutyl

borate, 3,5-difluorophenyl borate and pentafluorophenyl borate are preferable. These compounds are used alone or in combination of two or more species.

[0054]

5 Specific examples of the organoaluminum oxy compounds which react with such the alkyl borate include the same organoaluminum compounds listed as the organoaluminum compounds for the above general formula [2] or [3].

[0055]

10 Among these, trialkylaluminum and tricycloalkylaluminum are preferable, and trimethylaluminum, triethylaluminum, triisobutylaluminum, and diisobutylaluminum hydride are particularly preferable. These compounds are used alone or in combination of two or more species.

15 [0056]

(B-4) Compounds which react with the Group 4 transition metal compound (A) to form an ion pair

As the compounds (B-4) which react with the Group 4 transition metal compound (A) to form an ion pair, mention 20 may be made of Lewis acids, ionic compounds, borane compounds, carborane compounds and the like, as described in, for example, JP-A No. 1-501950, JP-A No. 1-502036, JP-A No. 3-179005, JP-A No. 3-179006, JP-A No. 3-207703, JP-A No. 3-207704, USP 5321106, etc.

25 [0057]

Specifically, the Lewis acids include the compound represented by BR_3 (wherein R is a phenyl group which may have a substituent such as fluorine, a methyl group and a trifluoromethyl group, or fluorine) such as, for example,

5 trifluoroboron, triphenyl boron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron, tris(3,5-dimethylphenyl)boron, trimethyl boron and triisobutyl boron

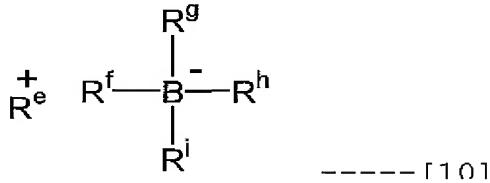
10 and the like.

[0058]

The ionic compounds include, for example, the compounds represented by the following general formula [10].

[0059]

15 [Chemical Formula 4]



[0060]

In the formula, examples of $\text{R}^{\text{e}+}$ include H^+ , a carbenium cation, an oxonium cation, an ammonium cation, a phosphonium cation, a cycloheptyltrietyl cation, a ferrocenium cation containing a transition metal, and the like. R^{f} to R^{i} may be the same or different from each other, and each represent an

organic group, and preferably an aryl group or a substituted aryl group.

[0061]

Specific examples of the carbenium cation include tri-
5 substituted carbenium cations such as a triphenylcarbenium cation, a tris(methylphenyl)carbenium cation, a tris(dimethylphenyl)carbenium cation, and the like.

[0062]

Specific examples of the ammonium cations include
10 trialkylammonium cations such as a trimethylammonium cation, a triethylammonium cation, a tri(n-propyl)ammonium cation, a triisopropylammonium cation, a tri(n-butyl)ammonium cation, and a triisobutylammonium cation; N,N-dialkylanilinium cations such as an N,N-dimethylanilinium cation, an N,N-
15 diethylanilinium cation, and an N,N-2,4,6-pentamethylanilinium cation; dialkylammonium cations such as a diisopropylammonium cation and a dicyclohexylammonium cation; and the like.

[0063]

20 Specific examples of the phosphonium cations include triarylphosphonium cations such as a triphenylphosphonium cation, a tris(methylphenyl)phosphonium cation, a tris(dimethylphenyl)phosphonium cation, and the like.

[0064]

25 Among them, R^e is preferably a carbenium cation, an

ammonium cation, or the like, and particularly preferably a triphenylcarbenium cation, an N,N-dimethylanilinium cation, or an N,N-diethylanilinium cation.

[0065]

5 Specific examples of the carbenium salts include triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(3,5-ditrifluoromethylphenyl)borate, tris(4-methylphenyl)carbenium tetrakis(pentafluorophenyl)borate,
10 tris(3,5-dimethylphenyl)carbenium tetrakis(pentafluorophenyl)borate, and the like.

[0066]

Examples of the ammonium salts include a tri-alkyl substituted ammonium salt, an N,N-dialkylanilinium salt, a
15 dialkylammonium salt, and the like.

[0067]

Specific examples of the tri-alkyl substituted ammonium salts include triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium
20 tetraphenylborate, trimethylammonium tetrakis(p-tolyl)borate, trimethylammonium tetrakis(o-tolyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(pentafluorophenyl)borate,
25 tripropylammonium tetrakis(2,4-dimethylphenyl)borate, tri(n-

butyl) ammonium tetrakis(3,5-dimethylphenyl)borate, tri(n-butyl) ammonium tetrakis(4-trifluoromethylphenyl)borate,
tri(n-butyl) ammonium tetrakis(3,5-ditrifluoromethylphenyl)borate, tri(n-butyl) ammonium
5 tetrakis(o-tolyl)borate, dioctadecylmethylammonium tetraphenylborate, dioctadecylmethylammonium tetrakis(p-tolyl)borate, dioctadecylmethylammonium tetrakis(o-tolyl)borate, dioctadecylmethylammonium tetrakis(pentafluorophenyl)borate, dioctadecylmethylammonium
10 tetrakis(2,4-dimethylphenyl)borate,
dioctadecylmethylammonium tetrakis(3,5-dimethylphenyl)borate,
dioctadecylmethylammonium tetrakis(4-trifluoromethylphenyl)borate, dioctadecylmethylammonium tetrakis(3,5-ditrifluoromethylphenyl)borate,
15 dioctadecylmethylammonium, and the like.

[0068]

Specific examples of the N,N-dialkylanilinium salts include N,N-dimethylanilinium tetraphenylborate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(3,5-ditrifluoromethylphenyl)borate, N,N-diethylanilinium
20 tetraphenylborate, N,N-diethylanilinium tetrakis(pentafluorophenyl)borate, N,N-diethylanilinium tetrakis(3,5-ditrifluoromethylphenyl)borate, N,N-2,4,6-pentamethylanilinium tetraphenylborate, N,N-2,4,6-

pentamethylanilinium tetrakis(pentafluorophenyl)borate, and the like.

[0069]

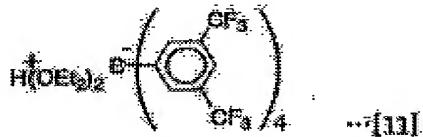
Specific examples of dialkylammonium salts include
5 di(1-propyl)ammonium tetrakis(pentafluorophenyl)borate,
dicyclohexylammonium tetraphenylborate, and the like.

[0070]

Additionally, mention may be made of ferrocenium
tetrakis(pentafluorophenyl)borate, a trisphenylcarbenium
10 pentaphenylcyclopentadienyl complex, an N,N-diethylanilinium
pentaphenylcyclopentadienyl complex, the borate compound
represented by the following formula [11] or [12], or the
borate compound containing an active hydrogen represented by
the following formula [13], the borate compound containing a
15 silyl group represented by the following formula [14], or
the like.

[0071]

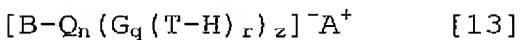
[Chemical Formula 5]



20 (wherein Et represents an ethyl group).

[0072]

[Chemical Formula 6]



[0073]

In the formula [13], B represents boron. G represents
5 a multi-binding hydrocarbon radical, examples of a
preferable multi-binding hydrocarbon include alkylene having
1 to 20 carbon atoms, arylene, ethylene or an alkalylene
radical, and preferable examples of G include phenylene,
bisphenylene, naphthalene, methylene, ethylene, propylene,
10 1,4-butadiene and p-phenylenemethylene. The multi-binding
radical G has r+1 bonds, that is, one bond binds to the
borate anion, and other r bonds of G bind to the (T-H)
groups. A⁺ represents a cation.

[0074]

15 In the formula [13], T represents O, S, NR^j or PR^j. R^j
represents a hydrocarbanyl radical, a trihydrocarbanylsilyl
radical, a trihydrocarbanylgermanium radical, or hydride. q
is an integer of at least 1, and preferably 1. As the T-H
group, mention may be made of -OH, -SH, -NRH or -PR^jH,
20 wherein R^j is a hydrocarbyl radical having 1 to 18 carbon
atoms, and preferably 1 to 10 carbon atoms, or hydrogen.
The R^j group is preferably alkyl, cycloalkyl, aryl,
arylalkyl, or alkylaryl having 1 to 18 carbon atoms. -OH, -

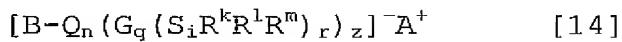
SH, -NRH or -PR^jH may be, for example, -C(O)-OH, -C(S)-SH-C(O)-NR^jH or C(O)-PR^jH. The most preferable group containing an active hydrogen is an -OH group. Q is hydride, dihydrocarbyl amide, and preferably dialkylamide, hydride, hydrocarbyloxide, alkoxide, allyloxide, a hydrocarbyl or substituted hydrocarbyl radical. In the formula, n+z is 4.

[0075]

As [B-Q_n(G_q(T-H)_r)_z] of the above formula [13], mention may be made of, for example, triphenyl(hydroxyphenyl)borate, diphenyl-di(hydroxyphenyl)borate, triphenyl(2,4-dihydroxyphenyl)borate, tri(p-tolyl)(hydroxyphenyl)borate, tris(pentafluorophenyl)(hydroxyphenyl)borate, tris(2,4-dimethylphenyl)(hydroxyphenyl)borate, tris(3,5-dimethylphenyl)(hydroxyphenyl)borate, tris[3,5-di(trifluoromethyl)phenyl](hydroxyphenyl)borate, tris(pentafluorophenyl)(2-hydroxyethyl)borate, tris(pentafluorophenyl)(4-hydroxybutyl)borate, tris(pentafluorophenyl)(4-hydroxycyclohexyl)borate, tris(pentafluorophenyl)[4-(4-hydroxyphenyl)phenyl]borate, tris(pentafluorophenyl)(6-hydroxy-2-naphthyl)borate, and the like, and most preferred is tris(pentafluorophenyl)(4-hydroxyphenyl)borate. Further, preferred is also the above borate compound in which the -OH group is substituted with -NHR^j (wherein R^j is methyl, ethyl or t-butyl).

25 [0076]

As A⁺ which is a countercation of the borate compound, mention may be made of a carbonium cation, a tropylium cation, an ammonium cation, an oxonium cation, a sulfonium cation, a phosphonium cation, and the like. Further, 5 mention may be made of positive ions of metals and positive ions of organometallics, which can easily be reduced. Specific examples of these cations include a triphenylcarbonium ion, a diphenylcarbonium ion, cycloheptatrinium, indenium, triethylammonium, tripropyl 10 ammonium, tributyl ammonium, dimethyl ammonium, dipropyl ammonium, dicyclohexyl ammonium, trioctyl ammonium, N,N-dimethyl ammonium, diethyl ammonium, 2,4,6-pentamethyl ammonium, N,N-dimethylphenyl ammonium, di-(i-propyl) ammonium, dicyclohexyl ammonium, triphenyl phosphonium, triphosphonium, 15 tridimethylphenyl phosphonium, tri(methylphenyl)phosphonium, a triphenyl phosphonium ion, a triphenyl oxonium ion, a triethyl oxonium ion, pyrinium, a silver ion, a gold ion, a platinum ion, a copper ion, a palladium ion, a mercury ion, a ferrocenium ion, and the like. Among these compounds, an 20 ammonium ion is particularly preferred.



[0077]

In the formula [14], B represents boron. G represents a multi-binding hydrocarbon radical, examples of a 25 preferable multi-binding hydrocarbon include alkylene having

1 to 20 carbon atoms, arylene, ethylene or an alkaylene radical, and preferable examples of G include phenylene, bisphenylene, naphthalene, methylene, ethylene, propylene, 1,4-butadiene and p-phenylenemethylene. The bonding of
5 multi-binding radical G is a $r+1$ bonding, that is, one bonding is bonded to a borate anion and another bonding r of G is bonded to the $(SiR^kR^lR^m)$ group. A⁺ represents a cation.

[0078]

R^k, R^l and R^m in the above general formula respectively
10 represent a hydrocarbanyl radical, a trihydrocarbanylsilyl radical, a trihydrocarbanylgermanium radical, a hydrogen radical, an alkoxy radical, a hydroxy radical or a halide radical. R^k, R^l and R^m may be the same or independent. Q represents hydride, dihydrocarbyl amide, preferably
15 dialkylamide, halide, hydrocarbyl oxide, alkoxide, allyloxide, a hydrocarbyl or substituted hydrocarbyl radical, and more preferably a pentafluorobenzyl radical. In the formula, n+z is 4.

[0079]

20 Examples of $[B-Q_n(G_q(S_iR^kR^lR^m)_r)_z]^-$ of the above formula
[14] include triphenyl(4-dimethylchlorosilylphenyl)borate,
diphenyl-di(4-dimethylchlorosilylphenyl)borate, triphenyl(4-dimethylmethoxysilylphenyl)borate, tri(p-tolyl)(4-triethoxysilylphenyl)borate, tris(pentafluorophenyl)(4-dimethylchlorosilylphenyl)borate, tris(pentafluorophenyl)(4-

dimethylmethoxysilylphenyl)borate,
tris(pentafluorophenyl) (4-trimethoxysilylphenyl)borate,
tris(pentafluorophenyl) (6-dimethylchlorosilyl-
2naphthyl)borate, and the like.

5 [0080]

Examples of A⁺ which is a countercation of the borate compound include the same A⁺ as those in the above formula [13].

[0081]

10 Specific examples of the borane compound include salts of anions such as decaborane (14), bis[tri(n-butyl)ammonium]nonaborate, bis[tri(n-butyl)ammonium]decaborate, bis[tri(n-butyl)ammonium]undecaborate, bis[tri(n-butyl)ammonium]dodecaborate, bis[tri(n-butyl)ammonium]dodecahydridedodecaborate, and bis [tri(n-butyl)ammonium]dodecahydridedodecaborate; salts of metal boran anions such as tri(n-butyl)ammonium bis(dodecahydridedodecaborate) cobaltate (III), and
15 bis[tri(n-butyl)ammonium]
bis(dodecahydridedodecaborate)nickelate (III); and the like.

20

[0082]

Specific examples of the carborane compound include salts of anions such as 4-carbanonaborane (14), 1,3-
25 dicarbanonaborane (13), 6,9-dicarbidecaborane (14),

dodecahydride-1-phenyl-1,3-dicarbanonaborane, dodecahydride-1-methyl-1,3-dicarbanonaborane, undecahydride-1,3-dimethyl-1,3-dicarbanonaborane, 7,8-dicarbaundecaborane (13), 2,7-dicarbaundecaborane (13), undecahydride-7,8-dimethyl-7,8-dicarbaundeca borane, undecahydride-11-methyl-2,7-dicarbaundeca borane, tri(n-butyl) ammonium-1-carbadecaborate, tri(n-butyl) ammonium-1-carbaundecaborate, tri(n-butyl) ammonium-1-carbadodecaborate, tri(n-butyl) ammonium-1-trimethylsilyl-1-carbadecaborate, tri(n-butyl) ammoniumbromo-1-carbadodecaborate, tri(n-butyl) ammonium-6-carbadecaborate (14), tri(n-butyl) ammonium-6-carbadecaborate (12), tri(n-butyl) ammonium-7-carbaundecaborate (13), tri(n-butyl) ammonium-7,8-dicarbaundecaborate (12), tri(n-butyl) ammonium-2,9-dicarbaundecaborate (12), tri(n-butyl) ammonium dodecahydride-8-methyl-7,9-dicarbaundecaborate, tri(n-butyl) ammoniumundecahydride-8-ethyl-7,9-dicarbaundecaborate, tri(n-butyl) ammonium undecahydride-8-butyl-7,9-dicarbaundecaborate, tri(n-butyl) ammonium undecahydride-8-allyl-7,9-dicarbaundecaborate, tri(n-butyl) ammonium undecahydride-9-trimethylsilyl-7,8-dicarbaundecaborate and tri(n-butyl) ammonium undecahydride-4,6-dibromo-7-carbaundecaborate; salts of metal carborane anions such as tri(n-butyl) ammonium bis(nonahydride-1,3-dicarbanonaborate)cobaltate (III), tri(n-butyl) ammonium bis(undecahydride-7,8-dicarbaundecaborate)ferrate (III),

tri(n-butyl)ammonium bis(undecahydride-7,8-dicarbaundecaborate)cobaltate (III), tri(n-butyl)ammonium bis(undecahydride-7,8-dicarbaundecaborate) nickelate (III),
5 tri(n-butyl)ammonium bis(undecahydride-7,8-dicarbaundecaborate) copperate (III), tri(n-butyl)ammonium bis(undecahydride-7,8-dicarbaundecaborate) aurate (III),
tri(n-butyl)ammonium bis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)ferrate (III), tri(n-butyl)ammonium
10 bis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate) chromate (III), tri(n-butyl)ammonium
bis(tribromo-octahydride-7,8-dicarbaundecaborate)cobaltate
(III), tris[tri(n-butyl)ammonium] bis(undecahydride-7-carbaundecaborate) chromate (III), bis[tri(n-butyl)ammonium]
15 bis(undecahydride-7-carbaundecaborate)manganate (IV),
bis[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate) cobaltate (III), and bis[tri(n-butyl)ammonium]bis(undecahydride-7-carbaundecaborate)nickelate (IV).

[0083]

20 Further, the compound (B) which reacts with the above Group 4 transition metal compound (A) to form an ion pair can be used in combination of two or more species.

In the polymerization, the method of using each component and the order of addition are chosen arbitrarily,
25 but the following methods are exemplified.

(1) Method of adding the component (A) only to a polymerization reactor.

(2) Method of charging the component (A) and the component (B) in an arbitrary order to a polymerization

5 reactor.

[0084]

In the above method (2), at least two of the respective catalyst components may be in contact with each other in advance.

10 [0085]

Monomers

In the invention, the olefins provided in polymerization reaction are one or more kinds of monomers selected from ethylene and α -olefins. As the α -olefins having 3 to 20 carbon atoms, and preferably 3 to 10 carbon atoms, mention may be made of include straight-chain or branched-chain α -olefins having 3 to 20 carbon atoms, such as propylene, 1-butene, 2-butenes, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, and the like. Also, in the polymerization method of the invention, mention may be made of cyclic olefins having 3 to 30 carbon atoms, and preferably 3 to 20 carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene,

tetracyclodecene, 2-methyl-1,4,5,8,-dimethanol-
1,2,3,4,4a,5,8,8a-octahydronaphthalene; polar monomers such
as acrylic acid, methacrylic acid, fumaric acid, maleic
anhydride, itaconic acid, itaconic anhydride, α,β -
5 unsaturated carboxylic acids such as bicyclo(2,2,1)-5-
heptene-2,3-dicarboxylic anhydride, etc. and metal salts
thereof such as a sodium salt thereof, a potassium salt
thereof, a lithium salt thereof, a zinc salt thereof, a
magnesium salt thereof and a calcium salt thereof; α,β -
10 unsaturated carboxylic acid esters such as methyl acrylate,
ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-
butyl acrylate, isobutyl acrylate, tert-butyl acrylate, 2-
ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate,
n-propyl methacrylate, isopropyl methacrylate, n-butyl
15 methacrylate and isobutyl methacrylate; vinyl ester such as
vinyl acetate, vinyl propionate, vinyl capronate, vinyl
caprate, vinyl laurate, vinyl stearate and vinyl
trifluoroacetate; unsaturated glycidyls such as glycidyl
acrylate, glycidyl methacrylate and monoglycidyl itaconate
20 esters; and the like. Also, polymerization may proceed
under the coexistence, in the reaction system, of vinyl
cyclohexane, diene or polyene; aromatic vinyl compounds, for
example, mono or polyalkylstyrene such as styrene, o-
methylstyrene, m-methylstyrene, p-methylstyrene, o,p-
25 dimethyl styrene, o-ethyl styrene, m-ethyl styrene and p-

ethyl styrene; styrene derivatives containing a functional group such as methoxy styrene, ethoxystyrene, vinylbenzoate, methyl vinylbenzoate, vinylbenzyl acetate, hydroxystyrene, o-chlorostyrene, p-chlorostyrene, divinylbenzene, and the like; and 3-phenylpropylene, 4-phenylpropylene, α -methylstyrene, and the like.

A solution polymerization method using a solvent known in the art or a high temperature and high pressure method can be employed as a polymerization method.

10 [0086]

Specific examples of the inert hydrocarbon medium used in the solution polymerization include aliphatic hydrocarbons such as propane, butane, pentane, heptane, hexane, octane, decane, dodecane and kerosene; alicyclic hydrocarbons such as cyclopentane, cyclohexane and methylcyclopentane; aromatic hydrocarbons such as benzene, toluene and xylene; halogenated hydrocarbons such as ethylene chloride, chlorobenzene, and dichloromethane; or a mixture thereof. Moreover, olefin as it is may be also used as a solvent.

20 [0087]

When olefin polymerization is carried out by using the catalyst for olefin polymerization as mentioned above, the component (A) is usually used in the amount in a range from 25 10^{-9} to 10^{-1} mole, and preferably from 10^{-8} to 10^{-2} mole with

respect to the reaction volume of 1 liter.

[0088]

The component (B-1) is used in such an amount that the molar ratio of the component (B-1) to the total transition metal atom (M) in the component (A), that is, $[(B-1)/M]$, is usually in the range from 0.01 to 5,000, and preferably from 0.05 to 2,000. The component (B-2) is used in such an amount that the molar ratio of the aluminum atoms in the component (B-2) to the total transition metal atom (M) in the component (A), that is, $[(B-2)/M]$, is usually in the range from 10 to 5,000, and preferably from 20 to 2,000. The component (B-3) is used in such an amount that the molar ratio of the component (B-3) to the transition metal atom (M) in the component (A), that is, $[(B-3)/M]$, is usually in the range from 1 to 100, and preferably from 1 to 50.

[0089]

The polymerization temperature in the solution polymerization is not particularly limited as long as it is 120°C or higher, but preferred is the range between 120 and 300°C, and more preferred is the range between 120 and 190°C because higher polymerization temperatures decrease the solution viscosity and promote heat removal in the polymerization. The polymerization is performed under the polymerization pressure usually in the range between the normal pressure and 10 MPa gauge, and preferably between the

normal pressure and 5 MPa gauge. The polymerization reaction can be carried out by using in any of batch, semi-continuous, and continuous modes. Also, the polymerization can be carried out by dividing the process into 2 or more 5 steps that are different in the polymerization conditions. The molecular weight of the obtained olefin polymer can also be controlled by incorporating hydrogen in the polymerization system, or by changing the polymerization temperature. Further, the molecular weight can be 10 controlled by the amount of the component (B) used. When hydrogen is added, it is suitable that the amount to be added is approximately in the range of between 0.001 and 10,000 NL per 1 kg of the olefin.

[0090]

15 Although not particularly limited in the olefin polymer prepared under the above condition, when performing polymerization according to the invention, the condition exhibiting the outstanding effects is such that a polymer having $MFR_{2.16}$ of 100 or less is prepared with a density of 20 0.92 g/cm³ or less, and further preferably such that a polymer having $MFR_{2.16}$ of 50 or less is prepared with a density of 0.915 g/cm³ or less.

[0091]

[Density]

25 By using a hydraulic hot press manufactured by Shinto

Metal Industries, Ltd. set at 190°C, first, a sheet with a thickness of 0.5 mm was formed at a pressure of 100 kg/cm² (nine 45 × 45 × 0.5 mm test specimens taken out of a spacer in the form of 240 × 240 × 0.5 mm in thickness). Then,
5 using a hydraulic hot press machine manufactured by Shinto Metal Industries, Ltd. set at 20°C, samples for measurement were prepared by pressing at a pressure of 100 kg/cm² while cooling. A SUS plate with a thickness of 5 mm was used as a hot plate.

10 [0092]

The pressed sheet was subject to heat treatment at 120°C for 1 hour, and slowly cooled linearly to room temperature over 1 hour, and then the density was measured using a density gradient tube.

15 [0093]

[Melt flow rate; MFR_{2.16}]

is a value determined according to a standard method of ASTM D-1238 at 190°C under a load of 2.16 kg.

[0094]

20 Hereinbelow, Examples will be described in detail without limiting the scope of the invention to these Examples.

[Example 1]

[0095]

25 Into a stainless-steel autoclave having an inner volume

of 2 liters which had been sufficiently replaced with nitrogen, 800 ml of hexane and 200 ml of 1-octene were charged. After raising the temperature of the autoclave content to 145°C, the total pressure was retained at 3 MPa-G by continuously supplying ethylene only. 0.3 mmol of triisobutylaluminum, 0.005 mmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 0.001 mmol of di(p-tolyl)methylene(cyclopentadienyl)(octamethyloctahydrodibenzo fluorenyl)zirconium dichloride were charged therein with nitrogen to initiate polymerization. The polymerization was performed at 150°C for 30 minutes. After stopping the polymerization by adding a small amount of ethanol to the reaction system, unreacted ethylene was purged. The obtained polymer solution was dried overnight at 80°C under reduced pressure. As a result, 68.0 g of an ethylene-1-octene copolymer was obtained with $MFR_{2.16} = 1.13$ (g/10 min) and a density of 0.893 (g/m³).

[Example 2]

[0096]

20 Into a stainless-steel autoclave having an inner volume of 2 liters which had been sufficiently replaced with nitrogen, 800 ml of hexane and 200 ml of 1-octene were charged. After raising the temperature of the autoclave content to 145°C, the total pressure was retained at 3 MPa-G by continuously supplying ethylene only. Next, 0.3 mmol of

triisobutylaluminum, 0.01 mmol of triphenylcarbenium tetrakis(pentafluorophenyl)borate and 0.002 mmol of di(p-tolyl)methylene(cyclopentadienyl)(octamethyloctahydrodibenzo fluorenyl)zirconium dichloride were charged therein with 5 nitrogen to initiate polymerization. The polymerization was performed at 150°C for 30 minutes. After stopping the polymerization by adding a small amount of ethanol to the reaction system, unreacted ethylene was purged. The obtained polymer solution was dried overnight at 80°C under 10 reduced pressure. As a result, 81.2 g of an ethylene-1-octene copolymer was obtained with $MFR_{2.16} = 2.09$ (g/10 min) and a density of 0.893 (g/m³).

[Example 3]

[0097]

15 Into a stainless-steel autoclave having an inner volume of 2 liters which had been sufficiently replaced with nitrogen, 800 ml of hexane and 200 ml of 1-octene were charged. After raising the temperature of the autoclave content to 145°C, the total pressure was retained at 3 MPa-G 20 by continuously supplying ethylene only. Next, 0.3 mmol of triisobutylaluminum, 0.005 mmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and 0.001 mmol of di(p-tolyl)methylene(cyclopentadienyl)(octamethyloctahydrodibenzo fluorenyl)zirconium dichloride were charged therein with 25 nitrogen to initiate polymerization. The polymerization was

performed at 150°C for 30 minutes. After stopping the polymerization by adding a small amount of ethanol to the reaction system, unreacted ethylene was purged. The obtained polymer solution was dried overnight at 80°C under 5 reduced pressure. As a result, 60.0 g of an ethylene-1-octene copolymer was obtained with $MFR_{2.16} = 0.67$ (g/10 min) and a density of 0.894 (g/m³).

[Name of Document] ABSTRACT

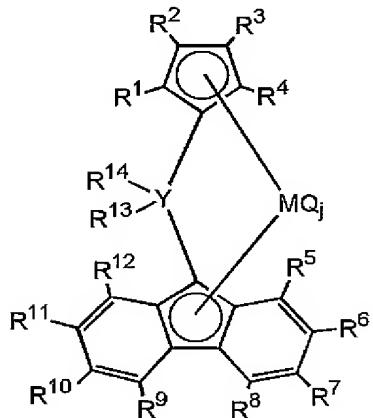
[Abstract]

[Object] The present invention provides a catalyst for copolymerization of a high molecular weight polymer under 5 the polymerization condition of high temperature.

[Solving Means] A process for producing an olefin polymer, which comprises polymerizing one or more kinds of monomers selected from ethylene and α -olefins at a temperature of 120°C or higher, in the presence of a catalyst for olefin 10 polymerization consisting of (A) a Group IVB transition metal compound represented by the following general formula [1]; and (B) at least one compound selected from the group consisting of

- (B-1) an organoaluminum oxy compound,
- 15 (B-2) a compound which reacts with the Group IVB transition metal compound (A) to form an ion pair, and
- (B-3) an organoaluminum compound.

[Chemical Formula 1]



[1]